

which have been published in the 'Philosophical Transactions' (vol. 179). It is illustrated partly by representations of certain of the brains showing the extent of the lesions, partly by photographs of microscopic sections through the spinal cord and medulla oblongata.

III. "On certain Ternary Alloys. I. Alloys of Lead, Tin, and Zinc." By C. R. ALDER WRIGHT, D.Sc., F.R.S., Lecturer on Chemistry and Physics, and C. THOMPSON, F.C.S., F.I.C., Demonstrator of Chemistry, in St. Mary's Hospital Medical School. Received March 5, 1889.

It is well known, that quite apart from a tendency to separate more or less completely into different mixtures during solidification, certain mixtures of molten metals show a tendency to separate into two alloys of different densities on standing fused for some time. Lead and zinc and bismuth and zinc have been shown by Matthiessen and von Bose ('Roy. Soc. Proc.,' vol. 11, p. 430) to form two such mixtures. We find that aluminium and zinc or aluminium and bismuth also behave in the same way. In each case two different alloys are formed, one consisting of the heavier metal with a little of the lighter one dissolved therein, the other of the lighter metal containing a small quantity of the heavier one.

On the other hand, *tin* will alloy indefinitely in all proportions with any one of the four metals, lead, bismuth, zinc, or aluminium, the mixtures exhibiting no particular tendency to separate into two different alloys on simply remaining at rest in a fused condition, although in certain cases more or less separation is apt to occur *during solidification*, owing to partial formation of eutectic alloy. On quickly cooling a mass of 60 to 80 grams of mixed metal, fused in a small narrow crucible and kept molten for some hours, an ingot is obtained, the highest and lowest portions of which exhibit sensibly the same composition on analysis; no more difference being observed than may reasonably be attributed to surface oxidation and volatilisation whilst standing molten, and to incipient formation of eutectic alloy during the act of solidification. Thus the following figures were obtained with two ingots of zinc and tin, and similarly in the other cases :—

	Zinc.	Tin.	Zinc.	Tin.
Top layer	31·13	68·87	61·14	38·86
Bottom layer	31·37	68·63	60·54	39·46
Mean.....	31·25	68·75	60·84	39·16

Various other metals, *e.g.*, cadmium, antimony, silver, &c., appear to behave like tin in this respect.

It occurred to us that it would be of interest to examine the behaviour under similar conditions of ternary mixtures where two of the ingredients are not miscible together in all proportions (like aluminium and lead), whilst the third is miscible indefinitely with either of the other two (like tin). *A priori*, it would seem probable that such mixtures would behave in a fashion similar to mixtures of alcohol, ether, and water. It is well known that these three fluids can be mixed together in certain proportions so as to form a single homogeneous liquid, not separating into two different layers on standing; whilst, on the other hand, certain mixtures of alcohol and ether, when agitated with water, ultimately form two different fluids, the heavier one consisting of water containing in solution some alcohol and ether, the lighter one of ether retaining the rest of the alcohol and some water. By parity of reasoning it might be expected that with certain proportions a single stable alloy would result, whilst with others the mass would divide into two different ternary mixtures. In point of fact this is precisely what occurs.

For a variety of reasons we selected the alloys of lead, tin, and zinc for our first experiments: these metals are easily obtained in quantity and of fair purity; the mixtures are fusible at temperatures easily attained and controlled; and the analysis of the resulting alloys is comparatively simple and easily executed with accuracy, no unimportant point when some 200 to 300 different alloys are to be examined, as we found to be ultimately necessary. Our first preliminary experiments indicated that when the lead and zinc are present in proportions not widely different (between the limits 3 to 1 and 1 to 3), the quantity of tin requisite to prevent separation into two different alloys was from $\frac{1}{3}$ to $\frac{2}{3}$ (33 to 40 per cent.) of the total mass, *i.e.*, such mixtures, after standing quiescent in a molten state for several hours and then cooled, gave ingots exhibiting sensibly the same composition at top and bottom. For example, the following figures were obtained with five different mixtures where the tin was always not less than 35 per cent. of the whole, whilst the zinc and lead varied in their ratio between the limits 1 to 2 and 2 to 1 or thereabouts:—

	Tin.	Lead.	Zinc.
Top	35·36	44·47	20·17
Bottom	35·80	43·62	20·58
Mean.....	35·58	44·05	20·37
Top	36·81	39·78	23·41
Bottom	37·91	39·41	22·68
Mean.....	37·36	39·60	23·04
Top	36·93	30·96	32·11
Bottom	38·23	31·84	29·93
Mean.....	37·58	31·40	31·02
Top	36·43	26·90	36·67
Bottom	36·90	27·93	35·17
Mean.....	36·67	27·41	35·92
Top	36·06	22·12	41·82
Bottom	37·58	23·05	39·37
Mean.....	36·82	22·59	40·59

These figures are the results of the analysis of the ingots obtained by melting the various mixtures in a crucible, well stirring together for some minutes, pouring into the red-hot bowl of a plugged clay tobacco-pipe, and keeping molten for some hours whilst at rest, and finally quickly cooling by removing the source of heat (a bunsen burner). The differences between the compositions of the top and bottom portions of the ingots are obviously no greater than what may be reasonably ascribed to surface oxidation and volatilisation, and possible slight variation introduced through partial separation into differently fusible alloys during solidification.

On the other hand, the following figures were obtained with three other mixtures, in which the tin constituted respectively about 9, 20, and 27 per cent. of the whole, whilst the zinc and lead were in the ratios 2 to 1, 1 to 1, and 1 to 2 in the three cases respectively:—

	Tin.	Lead.	Zinc.
Top	10·31	2·90	86·79
Bottom	7·70	90·22	2·08
Top	21·89	8·12	69·99
Bottom	18·48	75·76	5·76
Top	24·15	9·00	66·85
Bottom	29·56	53·20	17·24

These and various other similar experiments led us to the conclusion that the greater the proportion of tin present (provided it does not exceed the limiting amount beyond which no separation takes place) the more zinc is contained in the heavier alloy, and the more lead in the lighter one; but that the distribution of the tin throughout the entire mass is by no means uniform, the lighter alloy containing the greater percentage when the proportion of tin in the total mass is low, and *vice versa* when it approaches towards the limiting amount; so that with a particular proportion of tin in the total mass uniform distribution as regards weight percentage occurs, but with no other proportion.

These first indications appeared to be of sufficient interest to be worth following up by the examination of a large number of mixtures so as to enable curves to be drawn representing the variations in composition of the heavier and lighter alloys relatively to one another and in the distribution of the tin throughout the compound mass. Accordingly, we first of all attempted to find out whether a moderately large variation in the temperature at which the mass was kept molten had any great influence on the end result; for if not, obviously much laborious work would be saved, thermostats and arrangements for keeping constant temperatures for long periods of time together and such like devices, involving much complexity of working, being far less indispensable than would otherwise be the case. For this purpose we prepared two series of mixtures, in each of which equal quantities of lead and zinc were weighed up with varying quantities of tin. The metals were melted in a crucible (previously heated to a dull red heat) with a little cyanide of potassium, well stirred together with a clay rod for some minutes, and then poured into the red-hot bowl of a plugged clay tobacco-pipe and kept therein molten for four to five hours. In the first series the bowl was kept hot in the flame of a bunsen burner lapping all round the bowl; in the second, the heat was intensified by surrounding the bowl with a clay cylinder so as to jacket it. A bundle of pieces of thick platinum rod heated in exactly the same way and transferred to a calorimeter, gave with bowls not

jacketted temperatures varying in different experiments between 550° and 580° , and averaging exactly 565° ; whilst when heated in pipe bowls jacketted with the cylinder, temperatures were indicated varying between 675° and 705° , and averaging 689° , or 124° higher than before.* It may therefore be fairly assumed that the average temperature at which the mixtures were kept molten was not far from 124° higher in the second series than in the first.

After the requisite time had elapsed the lamp was removed, as also the jacketted cylinder when employed; in a few minutes the contents of the pipe-bowl were solid, when the clay was broken away from the somewhat conical compound ingot formed. After filing away about a couple of millimetres from the outside, the top and bottom portions were cut off by a cold chisel or saw and analysed. Usually a well-marked line of separation between the heavier and lighter alloys formed and was easily distinguishable; as long as the tin percentage in the total mass was low, this line was approximately in the middle of the mass, but with larger proportions of tin the dividing line gradually rose until the limit was being approached, beyond which no separation took place, when the dividing line was so near to the upper surface as to render it impossible to saw off even a thin layer of lighter alloy without intermixture with more or less of the heavier one.

The analysis in all cases was made as follows: a weighed portion (usually from 5 to 8 grams) was boiled with diluted pure nitric acid in a well-covered capacious beaker until complete oxidation was effected; the liquid was then diluted and allowed to stand till cold and filtered. No appreciable quantity of tin was ever found in solution.† The filtrate was evaporated to a small bulk with excess of pure sulphuric acid, and the lead sulphate produced collected and weighed; the filtrate and washings from this sometimes contained traces of lead; if so, these were precipitated by sulphuretted hydrogen

* The calorimeter employed contained a litre of water and had a water equivalent of 1050 grams; the thermometer read to $\frac{1}{100}$ of a degree centigrade. Taking the initial temperature of this calorimeter as t_1 , and the final as t_2 (corrected for radiation, &c.), W as the weight of platinum, and S its mean specific heat between t_2 and T, the temperature to be measured, the value of T was calculated by the formula

$$T = \frac{1050 \times (t_2 - t_1)}{W \cdot S} + t_2.$$

W in most of the observations was 51.055 grams; S was taken from Pouillet's values by interpolation as being

Between t_2 (about 15°) and 565	= 0.03545
" " 689	= 0.03595
" " 750	= 0.03625

† When tin is oxidised by dilute nitric acid in presence of relatively large quantities of certain metals, especially iron (*e.g.*, in the case of tinplate), very perceptible quantities of tin are generally taken permanently into solution.

and determined. Owing to the solution of lime, alumina, &c., from the vessels used during evaporation, we found that too high a value was always obtained by directly precipitating zinc with sodium carbonate from the acid fluid; wherefore we first precipitated it as sulphide by means of ammonia and ammonium sulphide, and redissolved the precipitate in dilute hydrochloric acid (after collection on a filter) before precipitating as carbonate. Any traces of zinc not thrown down thus were precipitated by adding a few drops of ammonium sulphide to the filtrate and thus estimated, whilst any traces of alumina and iron contained in the zinc oxide were determined and subtracted (after weighing) by dissolving in hydrochloric acid and supersaturating with ammonia. Usually these various filtrate and other corrections were all but infinitesimal: the analyses generally added up to 99·8 to 99·9 per cent., and the percentages finally quoted are usually reckoned upon the sum of the tin, lead, and zinc found as 100; in some cases, more especially with the lighter alloys, the tin and lead only were determined, the zinc being taken by difference.

Forty compound ingots (20 in each series) thus treated gave numbers concurring together reasonably well, furnishing the following averages; in several cases duplicate ingots were prepared, the mean values being those quoted.

Series I.—Temperature near 565°.

Heavier alloy.			Lighter alloy.			Excess of tin percentage in lighter alloy over that in heavier.
Tin.	Lead.	Zinc.	Tin.	Lead.	Zinc.	
0	98·70	1·30	0	1·10	98·90	0
1·79	96·86	1·35	2·49	1·80	95·71	0·70
4·67	93·69	1·64	7·31	3·17	89·52	2·64
7·66	89·77	2·57	10·97	4·67	84·36	3·31
8·99	88·04	2·97	13·04	5·70	81·26	4·05
12·15	84·19	3·66	16·50	6·28	77·22	4·35
16·66	78·98	4·36	20·63	7·10	72·27	3·97
18·10	76·57	5·33	21·75	7·30	70·95	3·65
21·36	71·34	7·30	24·09	8·58	67·33	2·73
25·81	61·33	12·86	26·28	9·92	63·80	0·47
29·60	54·90	16·50	27·91	10·95	61·14	−1·69
33·69	45·05	21·26	29·68	13·46	56·86	−4·01
34·98	49·37	24·65	29·84	14·26	55·90	−5·09
36·85	35·25	27·90	34·57	30·12	35·31	—

In each series the last mixture yielded so thin a layer of lighter alloy that it was impossible to saw off a sample free from admixture with a large amount of heavier alloy.

Series II.—Temperature near 689°.

Heavier alloy.			Lighter alloy.			Excess of tin percentage in lighter alloy over that in heavier.
Tin.	Lead.	Zinc.	Tin.	Lead.	Zinc.	
4·67	93·44	1·89	6·91	2·90	90·19	2·24
8·79	89·61	1·60	12·60	4·50	82·90	3·81
14·38	80·65	4·97	18·33	6·14	75·53	3·84
15·66	79·24	5·10	19·96	6·36	73·68	4·30
19·25	74·80	5·95	22·70	8·39	68·91	3·45
23·30	66·39	10·31	26·04	9·59	64·37	2·74
25·00	62·30	12·70	26·42	9·81	63·77	1·42
26·68	58·16	15·16	27·64	10·50	61·86	0·96
28·59	55·16	16·25	28·23	12·10	59·67	—0·36
31·11	49·92	18·97	27·76	11·68	60·56	—3·35
33·24	44·80	21·96	28·73	12·53	58·74	—4·51
34·99	37·67	27·34	29·20	14·45	56·35	—5·79
36·48	33·68	29·84	34·50	29·79	35·71	—

Besides these forty ingots, however, a number of others were obtained, yielding numbers on analysis not agreeing at all well with the forty, more especially as regards the lighter alloys. In all cases the figures were just such as would be obtained if complete separation by gravitation had not taken place, so that the lighter alloy retained a little of the heavier one disseminated through it, and *vice versa*; just as when ether and certain aqueous liquids are agitated together, a kind of froth forms, which takes a long time before it entirely separates, forming two clear liquids. As the experiments subsequently detailed render it certain that these abnormal ingots were simply cases where the separation was imperfect, the figures obtained with them are not included in the above tables, but it is obvious that this same source of error may have applied to a lesser extent even to some of the forty ingots not rejected. No doubt this was actually the case in some instances, on which account the curves obtained on plotting the above figures show a certain amount of sinuosity and irregularity. The error from this cause, however, as subsequently shown, is not serious; so that the concordance between the curves got from the two series of analyses respectively is sufficiently marked to show that no very considerable influence is exerted by a difference of temperature amounting to some 124°, on the way in which a given mass of lead, tin, and zinc divides itself on standing molten.

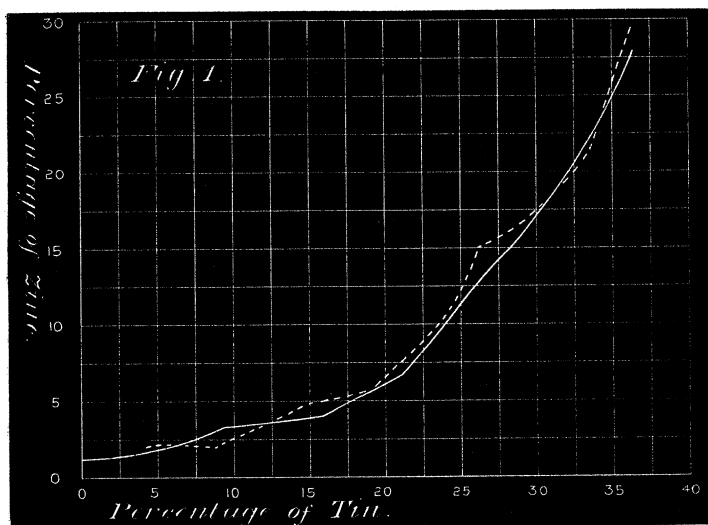
Three noteworthy curves are thus obtainable:—

(a.) When the tin percentages in the heavier alloy are plotted as abscissæ and the zinc percentages as ordinates.

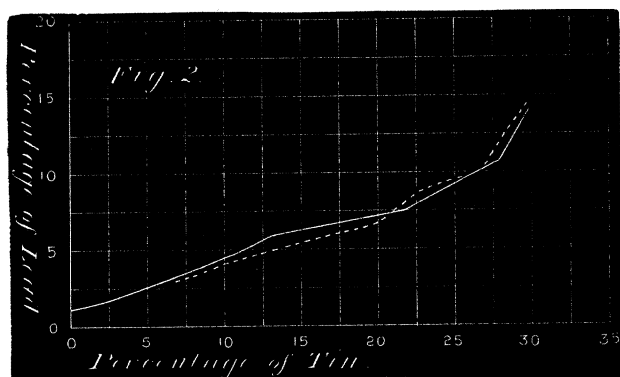
(b.) When the tin percentages in the lighter alloy are plotted as abscissæ and the lead percentages as ordinates.

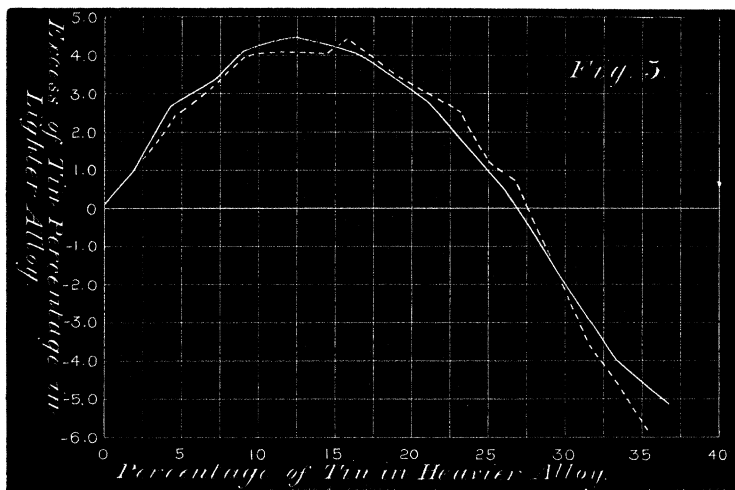
(c.) When the tin percentages in the heavier alloy are plotted as abscissæ and excesses of the percentage (+ or -) in the lighter alloy over those in the heavier one as ordinates.

These three curves respectively represent approximately the solubility of zinc in lead containing tin and that of lead in zinc containing tin, and the relative distribution of tin in the two alloys formed



simultaneously. Fig. 1 represents the two curves of the first kind plotted respectively from Series I and Series II, the continuous line





representing the first and the dotted line the second. Fig. 2 represents the corresponding curves of the second kind, and fig. 3 those of the third kind. Obviously, in each case there is little difference between the continuous and dotted lines, so that it may be fairly concluded that the effect of variation in temperature from 565° to 689° is negligible as compared with the experimental errors, more especially those due to imperfect separation by gravitation of the two alloys from one another.

The curves representing the distribution (fig. 3) are remarkable. As long as the tin percentage in the total mass is less than about sixteen the lighter alloy contains more tin than the heavier one; at about this point (representing some 14 per cent. in the heavier and 18 per cent. in the lighter alloy) the difference becomes a maximum after which the difference diminishes, until at about 28 per cent. the same percentage of tin is contained in both alloys. After this the heavier alloy contains more tin than the lighter, the difference continually increasing.

Causes retarding Separation of Lighter and Heavier Alloy.

Before proceeding further we thought it desirable to trace out the causes rendering separation incomplete, even after some hours' standing. At first we attributed it to the influence of traces of impurities in the metals used, but on repeating the observations in pipe-bowls with the purest samples of each metal obtainable, we still occasionally got irregular results, showing that this was not the sole cause. Next we thought that the error might be due to the partial formation of eutectic alloys during solidification, in such a way that

the portions of the ingots analysed did not truly represent the composition of the lighter and heavier alloys whilst molten. To avoid this we devised an arrangement whereby we could draw samples from the molten mass whilst still fluid. This consisted of a crucible holding some 500 to 600 grams of molten alloy, with a hole drilled through the bottom, closed by a conical plug worked up and down by means of a screw and lever. At the required moment, by turning the lever the plug could be slightly raised by the screw, so that a little of the lowest layer of molten metal escaped through the valve thus opened into an ingot mould placed to receive it. Simultaneously the top layer of molten metal could be sampled by a hot porcelain spoon. The crucible was surrounded by a cylindrical clay jacket to keep in the heat, which was supplied by a number of bunsen burners arranged so as to form a ring of flame between the crucible and jacket. Apparently there was no reason whatever why this arrangement should not work successfully; but in practice we did not succeed in getting, by its means, any results at all on which reliance could be placed. The analyses indicated that instead of this arrangement giving more complete separation than the pipe-bowls, it hardly ever gave so complete a one; on drawing samples at different times, instead of the separation gradually becoming more perfect as time elapsed, the opposite was often the case, some intermixing influence being apparently at work, which frequently was more powerful than the effect of gravitation in causing the lighter and heavier alloys to separate from one another. For instance, the following numbers were obtained in one experiment, indicating very incomplete separation as compared with the pipe-bowl results:—

Time.	Heavier alloy.			Lighter alloy.		
	Tin.	Lead.	Zinc.	Tin.	Lead.	Zinc.
5 hours	15·01	76·60	8·39	18·19	12·69	69·12
10 „	14·39	74·86	10·75	18·27	20·86	60·87

In another case no sensible separation at all was brought about after either four or eight hours with a mixture that separated readily when fused in a tall narrow crucible.

These particular two experiments are extreme cases as to irregularity; but still, in almost every instance, the figures obtained with the valve crucible were such as to show that the separation of heavier and lighter alloys from one another therein was extremely imperfect.

Valve Crucible.

	After 4 hours.			After 8 hours.		
	Tin.	Lead.	Zinc.	Tin.	Lead.	Zinc.
Top	25·30	24·48	50·22	26·30	24·16	49·30
Bottom	25·71	24·71	49·58	25·82	25·02	49·16

Tall narrow Crucible: 8 hours.

	Tin.	Lead.	Zinc.
Top	27·83	9·81	62·36
Bottom	25·63	62·39	11·98

In these cases it was clear that the formation of eutectic alloys during solidification was not the cause of the irregularities observed, whence presumably the same is true for the less irregular results obtained with the pipe-bowls. Ultimately we traced the cause to convection currents set up through unequal heating of the walls of the containing vessels at different levels, and found that the imperfect separation could be almost completely obviated by so heating the mass as to avoid this inequality of temperature. This we ultimately effected by employing crucibles very long in proportion to their diameter (large test-tubes moulded on a core from a plastic mixture of fireclay and syrupy silicate of soda, diluted with about three times its weight of water), heated by immersion in a bath of molten lead some 8 or 9 inches deep, contained in an iron cylindrical vessel (the lower two-thirds of a mercury bottle), surrounded by a concentric clay jacket and heated by a number of bunsen burners playing into the annular interspace. The molten metals being well intermixed in a crucible (with a little potassium cyanide), the mixture was poured into a red-hot clay test-tube, which was then quickly transferred to the hot lead-bath, the mouth of the tube being covered with a heavy iron cap so as to depress the test-tube into the lead to such a depth that the top of the molten metal inside was some 2 inches below the surface of the lead in the bath whilst the tube was kept vertical. Under these conditions, practically complete separation was always brought about after six to eight hours in the lead-bath. Usually several test-tubes were heated simultaneously. After the required time had elapsed they were carefully lifted out without shaking, and set by to cool, still in a vertical

position. To diminish oxidation, a reducing atmosphere was maintained in the upper part of the lead-bath by covering it loosely with a lid and passing a jet of coal-gas inside. In some few instances the test-tubes were not weighted down with iron caps, so that the level of the metal inside was *above* the top of the lead; under these circumstances the upper part of the metal was largely heated by convection, and in all such cases it was found that the lighter alloy retained some of the heavier alloy interspersed through it, the convection currents preventing complete separation by gravitation. Thus, for example, two similar mixtures, containing about 23·5 per cent. of tin, were heated simultaneously for eight hours, one completely depressed so as to avoid convection currents, the other raised so as to ensure their production, with the following results:—

	Heavier alloy.			Lighter alloy.		
	Tin.	Lead.	Zinc.	Tin.	Lead.	Zinc.
Depressed	22·32	69·84	7·84	25·71	8·84	65·44
Raised	22·50	68·89	8·61	24·16	17·44	58·40

The figures obtained with the depressed tube are perfectly normal (*vide infra*), whilst those obtained with the other are such as to show that, owing to the convection currents set up, a little of the lighter alloy was still intermixed with the heavier, whilst a considerable amount of the heavier one was interspersed throughout the lighter one.

Lead-bath Observations.

As a check on the curves above described obtained with pipe-bowls, we made another similar series of observations with mixtures containing equal quantities of lead and zinc and varying proportions of tin, employing clay test-tubes heated in a lead-bath. The temperature of the bath was ascertained from time to time by heating a bundle of thick platinum rods in a clay test-tube in the bath and transferring it to the calorimeter; the temperatures thus observed lay between 610° and 710°, with an average of 646° for the whole series of ingots, twenty-two of which were prepared, not one giving any markedly abnormal results on analysis. The following figures were obtained, several of the ingots being duplicates and the mean figures being quoted. In all cases the time during which the mass remained molten was about eight hours.

Series III.—Lead-bath. Temperature near 646°.

Heavier alloy.			Lighter alloy.			Excess of tin percentage in lighter alloy over that in heavier.
Tin.	Lead.	Zinc.	Tin.	Lead.	Zinc.	
0	98·70	1·30	0	1·17	98·83	0
4·77	93·67	1·56	7·17	2·17	90·66	2·40
6·42	91·96	1·62	9·81	2·78	87·41	3·39
9·85	87·70	2·45	13·36	3·49	83·15	3·51
13·06	83·70	3·24	17·13	4·04	78·83	4·07
13·77	82·42	3·81	18·37	4·54	77·09	4·60
15·30	79·90	4·80	19·61	5·29	75·10	4·31
22·32	69·84	7·84	25·72	8·84	65·44	3·40
26·99	60·08	12·93	28·22	10·49	61·29	1·23
28·57	56·51	14·92	28·55	11·63	59·82	-0·02
30·87	52·47	16·66	28·90	11·66	59·44	-1·98
32·86	46·94	20·20	30·13	13·19	56·68	-2·73
34·76	42·43	22·81	30·19	13·80	56·01	-4·57
35·38	40·07	24·55	29·76	13·81	56·43	-5·62

On plotting these numbers as before, it is at once evident that the curves thence obtained differ but little from those obtained in Series I and II, excepting in being more regular, what differences exist being such as are obviously due to the more nearly complete separation now obtained in all cases; whence it may reasonably be inferred that the conclusion previously arrived at is correct, viz., that a variation in temperature between 565° and 689° makes practically no difference in the way in which a given mass of metal divides itself on standing molten. This conclusion is corroborated by the results described below, obtained with two other series of mixtures containing lead and zinc in the proportion 1 to 2, in the first of which a mean temperature close to 650° was employed, and in the second a temperature about 100° higher; the curves deduced from the two series respectively differing from one another only by amounts barely, if at all, outside the limits of experimental error.

Experiments with Lead and Zinc in Unequal Proportions.

We next made several series of observations with lead and zinc in unequal proportions and varying quantities of tin, with the object of finding out how far the distribution of tin between the two resulting alloys is influenced by the relative masses of metals present. If the alloys formed when completely separated from one another are respectively saturated solution of zinc in lead containing tin (bottom) and saturated solution of lead in zinc containing tin (top), it should result that the two first curves obtained as above described will be the

same no matter what may be the relative proportions of zinc and lead in the total mass; and this, in point of fact, we find to be the case. But it does not follow therefrom that with a mass of metal containing x per cent. of tin the same pair of alloys will be obtained, no matter in what relative proportions the zinc and lead may exist in the remaining $100-x$ per cent.; and, in point of fact, we find not only that a different pair results for each variation in the relative proportions of zinc and lead in such a case, but, further, that the curves representing the relative distribution of tin in the two alloys are not the same for all proportions between zinc and lead in the total mass. When zinc predominates the curve rises less rapidly, the maximum difference in tin percentage is attained later, and the point of equal distribution of tin throughout the entire mass lies further from the origin than when the zinc and lead are present in equal proportions in the entire mass; and *vice versa* when lead predominates.

Thus the following values were obtained from a series of sixteen compound ingots, prepared in the lead-bath at an average temperature of close to 650° , the masses remaining fused for about eight hours in each case, the proportions between zinc and lead in the metals weighed up being uniformly 2 to 1.

Series IV.—Zinc double the Lead present. Temperature near 650° .

Heavier alloy.			Lighter alloy.			Excess of tin percentage in lighter alloy over that in heavier.
Tin.	Lead.	Zinc.	Tin.	Lead.	Zinc.	
0	98·78	1·22	0	1·08	98·92	0
3·67	94·39	1·94	5·17	2·21	92·62	1·50
7·70	90·22	2·08	10·31	2·90	86·79	2·59
10·81	86·42	2·77	14·74	3·71	81·55	3·98
14·85	81·40	3·75	19·48	5·22	75·30	4·63
16·36	79·24	4·40	21·09	5·97	72·94	4·73
18·79	75·62	5·59	23·07	6·67	70·26	4·28
20·19	74·03	5·78	24·11	6·98	68·91	3·92
25·63	62·39	11·98	27·83	9·81	62·36	2·20
28·70	54·76	16·54	28·80	10·76	60·44	0·10
30·58	51·01	18·41	29·39	11·82	58·79	-1·19
..	..	..	29·80	12·24	57·96	..
33·49	44·21	22·30	31·35	13·55	55·10	-2·14
35·34	37·06	27·60	32·03	15·57	52·40	-3·31

A similar series of eight ingots at a higher temperature, close to 750° , gave the following results:—

Series V.—Zinc double the Lead present. Temperature near 750°.

Heavier alloy.			Lighter alloy.			Excess of tin percentage in lighter alloy over that in heavier.
Tin.	Lead.	Zinc.	Tin.	Lead.	Zinc.	
5·96	92·10	1·94	8·53	3·18	88·29	2·57
10·76	86·29	2·95	14·87	3·69	81·44	4·11
16·58	78·43	4·99	20·44	6·00	73·56	3·86
22·57	70·79	6·64	25·41	7·05	67·54	2·84
29·41	52·75	17·84	29·34	11·71	58·95	—0·07
31·95	46·73	21·32	31·02	13·49	55·49	—0·93
34·24	42·28	23·48	31·70	13·74	54·56	—2·54
34·78	40·23	24·99	32·16	15·21	52·63	—2·62

On plotting these two series it is obvious that the curves are practically identical in both cases; indicating, as above shown, that little, if any, sensible difference is brought about by a considerable temperature variation in the way in which a given mass of metal divides itself on standing. On the other hand, whilst the solubility curves of zinc in lead-tin and of lead in zinc-tin thence derived are sensibly the same as those derived from Series III, the tin distribution curves are by no means identical therewith, especially with the highest tin percentages.

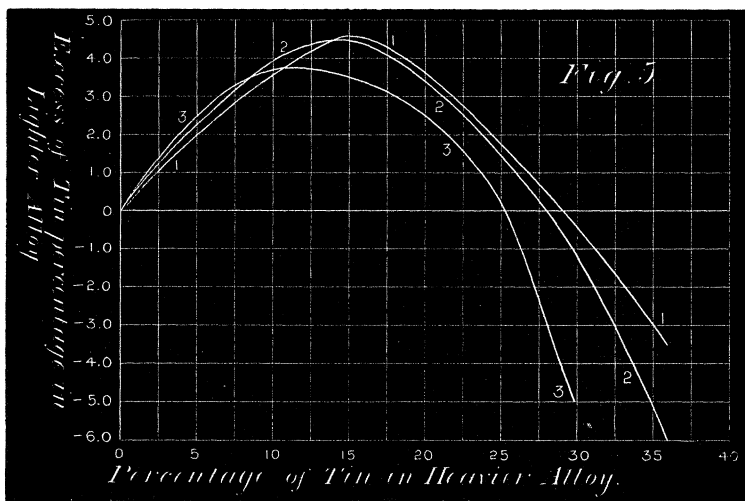
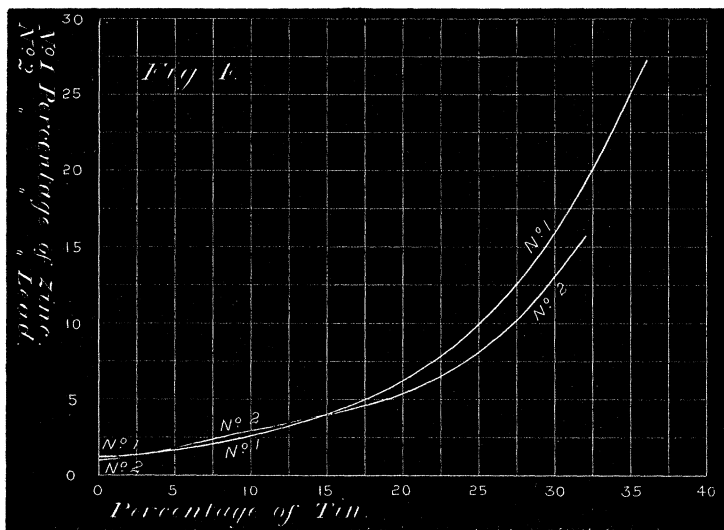
Another series of mixtures was then prepared with zinc and lead in the proportions 1 to 2. The following values were obtained from twenty ingots fused about eight hours at a temperature close to 650°.

Series VI.—Lead double the Zinc present. Temperature near 650°

Heavier alloy.			Lighter alloy.			Excess of tin percentage in lighter alloy over that in heavier.
Tin.	Lead.	Zinc.	Tin.	Lead.	Zinc.	
0	98·86	1·14	0	1·22	98·78	0
5·38	92·82	1·80	8·20	2·25	89·55	2·82
9·06	89·03	1·91	12·44	3·36	84·20	3·38
11·27	86·23	2·50	14·94	3·92	81·14	3·67
15·40	80·78	3·82	18·70	5·19	86·11	3·30
19·92	74·11	5·97	..	..	..	..
21·24	71·70	7·06	23·32	7·38	69·30	2·08
22·78	68·85	8·37	24·21	7·80	67·99	1·43
25·28	64·00	10·72	25·31	8·29	66·40	—0·03
26·48	58·96	14·56	24·67	7·95	67·38	—1·81
29·66	54·99	15·35	25·03	8·20	66·77	—4·63
31·02	50·92	18·06	25·40	8·70	65·90	—5·62

On plotting these numbers it becomes evident that whilst the solubility curves of zinc in lead-tin and of lead in zinc-tin thence derived are sensibly identical with those obtained from Series III, IV, and V, the tin distribution curve is different from either of those obtained with zinc and lead in the proportions 1 to 1 and 2 to 1.

Fig. 4 represents the mean solubility curves (1) for zinc in lead-tin, (2) for lead in zinc-tin, derived from all the foregoing observations



made in the lead-bath, the abscissæ being in each case tin percentages, and the ordinates zinc percentages for curve No. 1, and lead percentages for curve No. 2. The two curves are not widely different at first, but latterly curve No. 1 distinctly overlies No. 2.

Fig. 5 represents the mean tin distribution curves derived from the preceding observations, No. 1 being that derived from the experiments where the zinc present was double the lead, No. 2 where the two metals were in equal proportions, and No. 3 where the lead was double the zinc. The maxima obtained correspond respectively with the ordinate values 4·7, 4·6, and 3·7, and are situated at about the abscissa values 15, 14, and 12 respectively. The crossing points (points of equal tin distribution as regards weight percentage through the mass) are respectively close to 29·0, 28·5, and 25·2 per cent. of tin. The gradient of rise towards the maximum and of fall subsequently below the crossing point is steepest in curve No. 3 and least steep in No. 1.

The following tables contain the mean values graphically represented by these curves.

Solubility of Zinc in Lead-tin.			Solubility of Lead in Zinc-tin.		
Per cent. of tin.	Per cent. of zinc.	Difference.	Per cent. of tin.	Per cent. of lead.	Difference.
0	1·24	0·20	0	1·14	0·33
2	1·44	0·21	2	1·47	0·33
4	1·65	0·24	4	1·80	0·33
6	1·89	0·26	6	2·13	0·33
8	2·15	0·30	8	2·46	0·34
10	2·45	0·40	10	2·80	0·34
12	2·85	0·55	12	3·14	0·36
14	3·4	0·7	14	3·50	0·40
16	4·1	0·9	16	3·9	0·6
18	5·0	1·1	18	4·5	0·8
20	6·1	1·4	20	5·3	1·0
22	7·5	1·75	22	6·3	1·2
24	9·25	2·0	24	7·5	1·4
26	11·25	2·25	26	8·9	1·7
28	14·5	2·5	28	10·6	2·15
30	17·0	2·75	30	12·75	2·75
32	19·75	3·25	32	15·5	
34	23·0	4·0			
36	27·0				

Tin Distribution Curves.

Percentage of tin in heavier alloy.	Excess of tin percentage in lighter alloy over that in heavier.					
	Zinc double the lead.		Equal.		Lead double the zinc.	
	Difference.		Difference.		Difference.	
2	0·8	0·8	0·9	0·9	1·1	1·1
4	1·6	0·8	1·8	0·9	2·2	1·1
6	2·4	0·8	2·7	0·9	2·9	0·7
8	3·1	0·7	3·4	0·7	3·3	0·4
10	3·7	0·6	3·9	0·5	3·55	0·25
12	4·2	0·5	4·35	0·45	3·7	0·15
14	4·55	0·35	4·6	0·25	3·55	-0·15
15	4·7	0·15	..	..	..	..
16	4·55	-0·15	4·35	-0·25	3·3	-0·25
18	4·2	-0·35	4·0	-0·35	3·0	-0·3
20	3·75	-0·45	3·6	-0·4	2·5	-0·5
22	3·1	-0·65	3·0	-0·6	1·75	-0·75
24	2·3	-0·8	2·2	-0·8	0·75	-1·0
25·2	..	..	..	..	0	..
26	1·4	-0·9	1·3	-0·9	-0·8	-1·55
28	0·45	-0·95	0·25	-1·05	-2·7	-1·9
28·5	..	..	0	..	..	..
29	0	..	..	..	..	..
30	-0·5	-0·95	-1·10	-1·35	-4·9	-2·2
32	-1·5	-1·0	-2·66	-1·56	..	..
34	-2·5	-1·0	-4·33	-1·67	..	..
36	-3·5	-1·0	-6·0	-1·67	..	..

Miscibility of Lead and Zinc in the Absence of Tin.

It is worth noticing that four sets of ingots have been examined above, with the following results:—

	Heavier alloy.		Lighter alloy.	
	Lead.	Zinc.	Lead.	Zinc.
Pipe-bowl.....	98·70	1·30	1·10	98·90
Lead-bath, zinc double the lead	98·78	1·22	1·08	98·92
„ equal.....	98·70	1·30	1·17	98·83
„ lead double the zinc.....	98·86	1·14	1·22	98·78
Mean.....	98·76	1·24	1·14	99·86

These values are somewhat lower as regards the zinc dissolved by lead, and *vice versa*, than the figures given by Matthiessen and

v. Bose (*loc. cit. supra*), which lead to the percentages 1.62—1.79 of zinc in heavier alloy, mean = 1.67; and 1.17—1.22 of lead in lighter alloy, mean = 1.20. Obviously this arises from the fact that the method of working adopted by Matthiessen and v. Bose did not allow of so complete a separation taking place as was effected in our experiments, as they employed a far shorter time.

Variation in mean Composition through Oxidation and Volatilisation.

In melting and mixing together the metals employed, it is quite impossible to avoid some loss by oxidation, even when a luminous gas flame is directed into the crucible so as to maintain a reducing atmosphere therein. Moreover, some amount of volatilisation, especially of zinc, takes place, owing to prolonged heating at 650—750°. A number of observations made with mixtures that did not separate into two alloys showed that the total quantity of tin in the final ingot is but little, if at all, less than that originally weighed up; some lead is lost and more zinc, roughly averaging about twice as much as the lead. The total amount of loss, however, even after eight hours' heating, is not very great; as a rule, ingots were made for which about 80 grams of total metal were weighed up; the weight of final compound ingot was generally near to 77 grams (excluding mechanical losses during stirring and transference to the clay test-tubes), about 3 grams representing the loss by oxidation and volatilisation. In a few cases a larger amount of oxidation took place, but comparatively rarely with careful handling. The result of this action is to cause an increment in the mean percentage of tin in the mass to the extent of something like one twenty-fifth of its value (*i.e.*, a mass originally containing 25 per cent. of tin will ultimately contain about 26). Simultaneously the ratio of zinc to lead is altered; only to a small extent if these metals were originally in the proportion of 2 to 1, but relatively more if the zinc were present to a lesser extent.

In the foregoing experiments the proportions subsisting between zinc, lead, and tin referred to are uniformly those in which the metals were *weighed up for use*, and consequently not quite the same as those actually subsisting in the compound ingots finally obtained; these latter probably contained zinc and lead in ratios near to 2 to 1, 0.96 to 1, and 0.46 to 1, respectively, on the average.

Summary of Results.

When a mixture of lead, tin, and zinc in the molten condition is well stirred up by mechanical means and then left to itself for some hours at as nearly as possible a uniform temperature, a single homogeneous alloy results if the proportion of tin present is not less than three-eighths of the whole; but if materially less tin than this is

present, the mass divides itself into two different ternary alloys, lead predominating in the heavier one and zinc in the lighter one. This phenomenon is entirely distinct from the segregation of alloys during solidification, in consequence of formation of eutectic or other differently fusible alloys.

If there is little or no inequality of temperature at different parts of the mass, separation by gravitation only is complete in a few hours, at any rate when tolerably pure metals are employed; but if the mode of heating is such that convection currents are set up, the separation is greatly interfered with, and in extreme cases almost entirely prevented.

The heavier alloy is a saturated solution of zinc in lead containing tin, and the lighter one a similar solution of lead in zinc containing tin. No matter what the relative proportions between lead and zinc in the original mass, the two alloys always correspond to two conjugate points on the solubility curves of zinc in lead-tin and of lead in zinc-tin.

But little, if any, difference in the way in which a given mass divides itself is noticeable, whether the temperature at which the molten mass is maintained is below 600° C. or above 700° C.

The tin contained in the mass does not distribute itself equally in the two alloys except when present in one particular proportion, which varies with the ratio of the zinc to the lead in the entire mass. With less tin than this the lighter alloy, and with more the heavier one, takes up the higher percentage of tin.

Curves drawn representing the tin present in the heavier alloy as abscissæ, and the (+ or -) excess of tin in the lighter alloy over that in the heavier one as ordinates, are found to differ with the ratio of zinc to lead in the entire mass. They always possess the same general features, viz., rising from the origin to a maximum elevation, then sinking down again to the base line, and crossing it so as to become negative; but the position and height of the maximum, the crossing point, and the general dimensions of the curve vary with the ratio of zinc to lead in the mass.

As a result of this, whilst an indefinite number of different mixtures may be prepared, each one of which will give the same heavier alloy, the lighter alloy simultaneously formed will be different in each case; and conversely.

When no tin is present, lead dissolves zinc to such an extent as to form an alloy containing 1.24 per cent. of zinc, and zinc dissolves lead forming an alloy containing 1.14 per cent. of lead; the higher values found by previous observers being slightly incorrect through imperfect separation.

Before attempting to theorise on the causes leading to the remarkable way in which tin is distributed in these ternary alloys, we desire

to accumulate additional data derived from the examination of other parallel cases, such as the ternary alloys obtained by adding tin to the immiscible pairs of metals, zinc and bismuth, aluminium and lead, and aluminium and bismuth; or by similarly employing other metals instead of tin. Nothing abnormal appears to characterise the solubility curves of zinc in lead-tin and of lead in zinc-tin; in each case the amount of one metal dissolved by the other increases as the quantity of tin present increases, in such a way that the curves are somewhat concave upwards.

IV. "The Diurnal Variation of Terrestrial Magnetism." By ARTHUR SCHUSTER, F.R.S., Professor of Physics, with an Appendix by H. LAMB, F.R.S., Professor of Mathematics, Owens College, Manchester. Received March 20, 1889.

(Abstract.)

In the year 1839 Gauss published his celebrated Memoir on Terrestrial Magnetism, in which the potential on the earth's surface was calculated to twenty-four terms of a series of surface harmonics. It was proved in this memoir that if the horizontal components of magnetic force were known all over the earth the surface potential could be derived without the help of the vertical forces, and it is well known now how these latter can be used to separate the terms of the potential which depend on internal from those which depend on external sources. Nevertheless, Gauss made use of the vertical forces in his calculations of the surface potential, in order to ensure a greater degree of accuracy. He assumed for this purpose that magnetic matter was distributed through the interior of the earth, and mentions the fair agreement between calculated and observed facts as a justification of his assumption. In the latter part of the memoir it was suggested that the same method should be employed in the investigation of the regular and secular variations.

The use of harmonic analysis to separate internal from external causes has never been put to a practical test, but it seems to me to be specially well adapted to inquiries on the causes of the periodic oscillations of the magnetic needle.

If the magnetic effects can be fairly represented by a single term in the series of harmonics as far as the horizontal forces are concerned, there should be no doubt as to the location of the disturbing cause, for the vertical force should be in the opposite direction if the origin is outside from what it should be if the origin is inside the earth. As the expression for the potential contains in one case the distance from the earth's centre in the numerator, in the other case in the denominator, and as the vertical force depends on the diffe-

Fig 1.

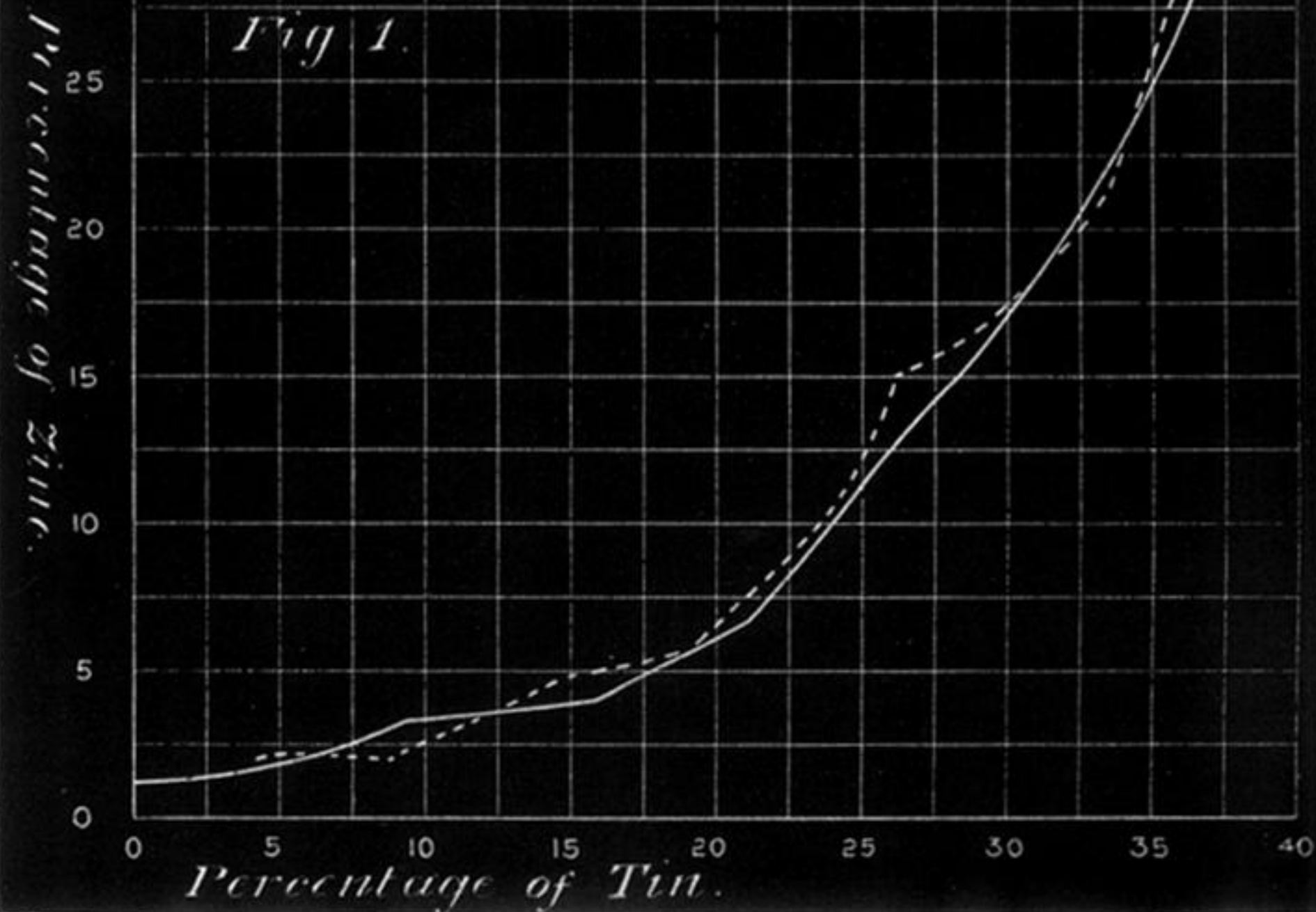
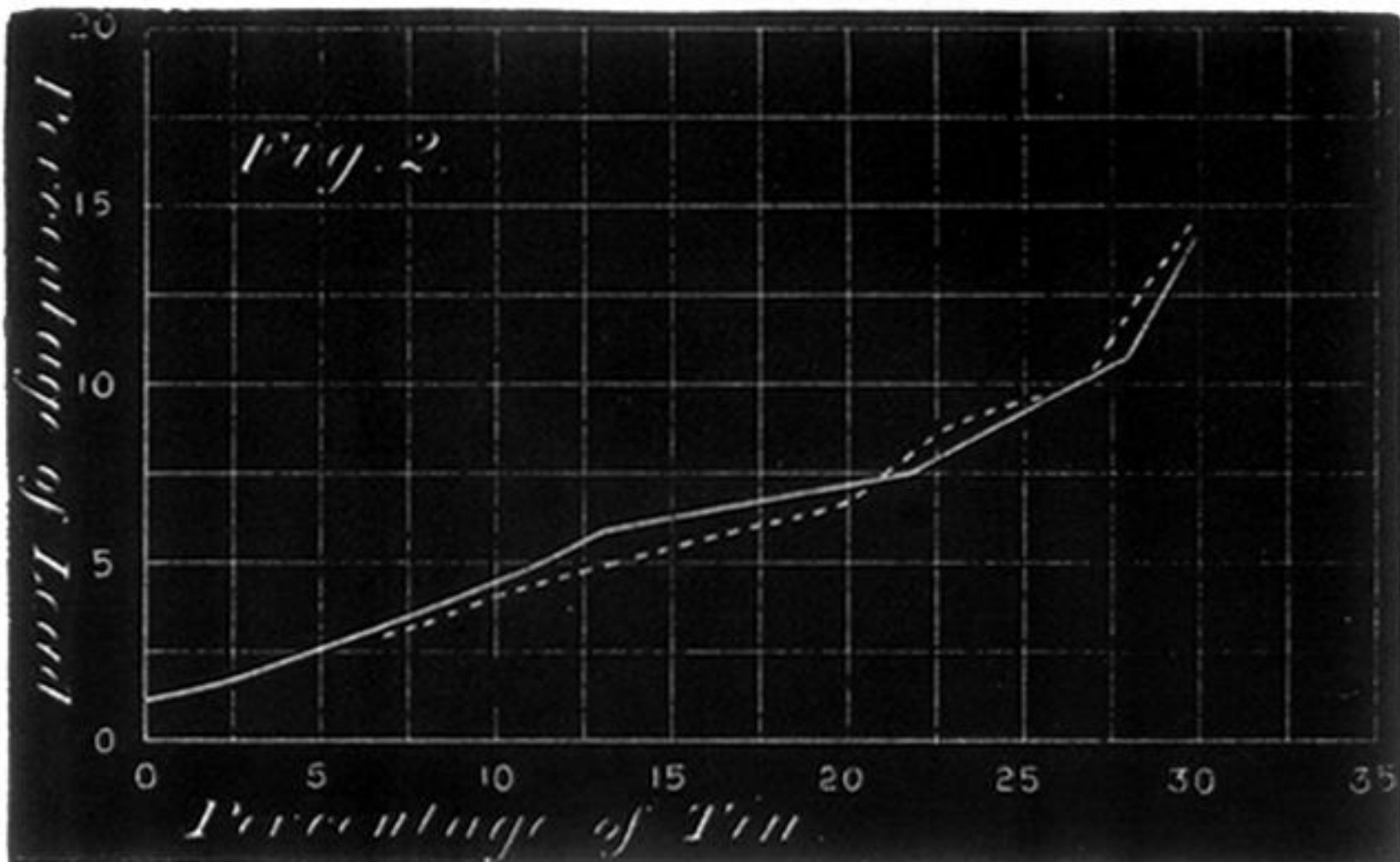
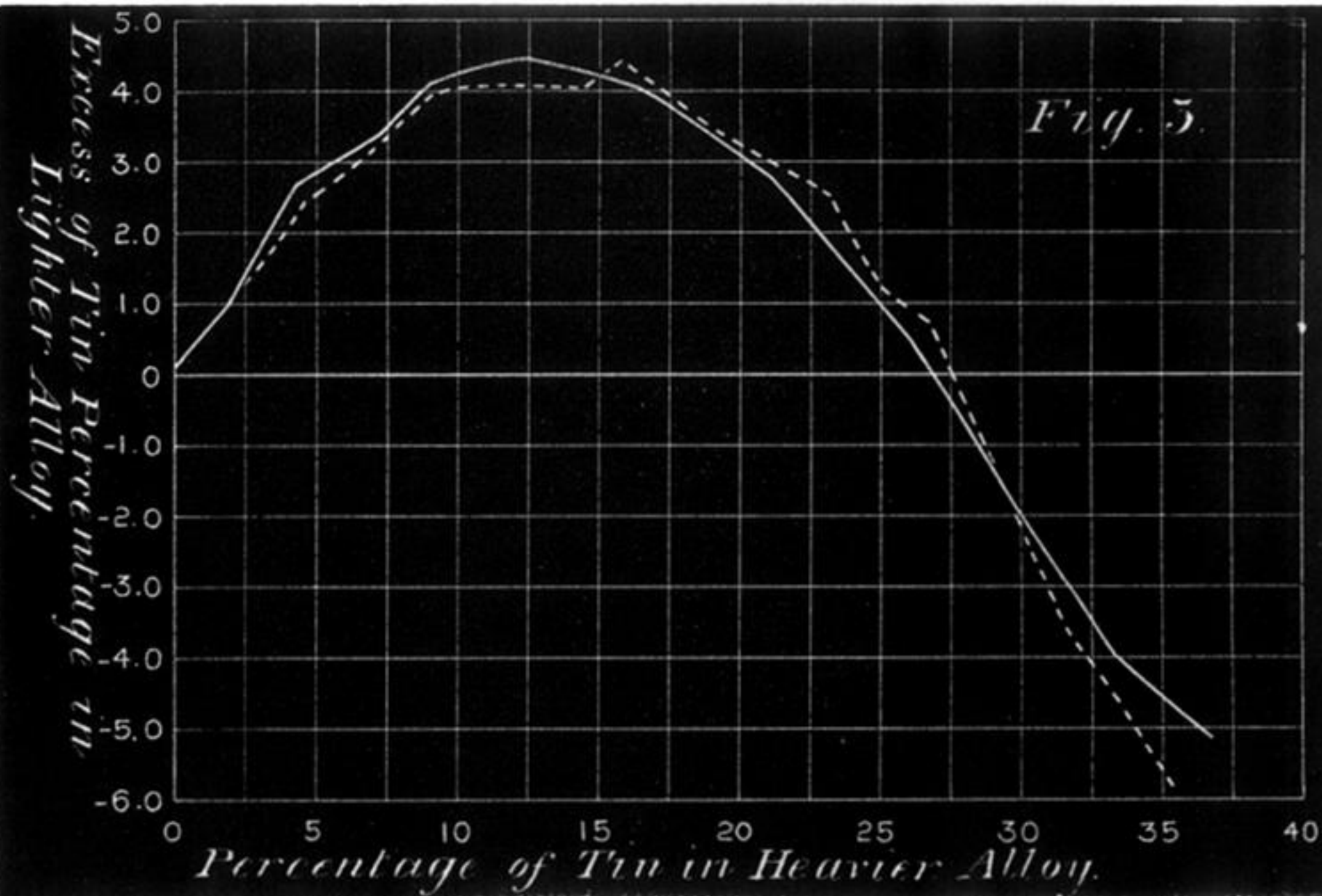


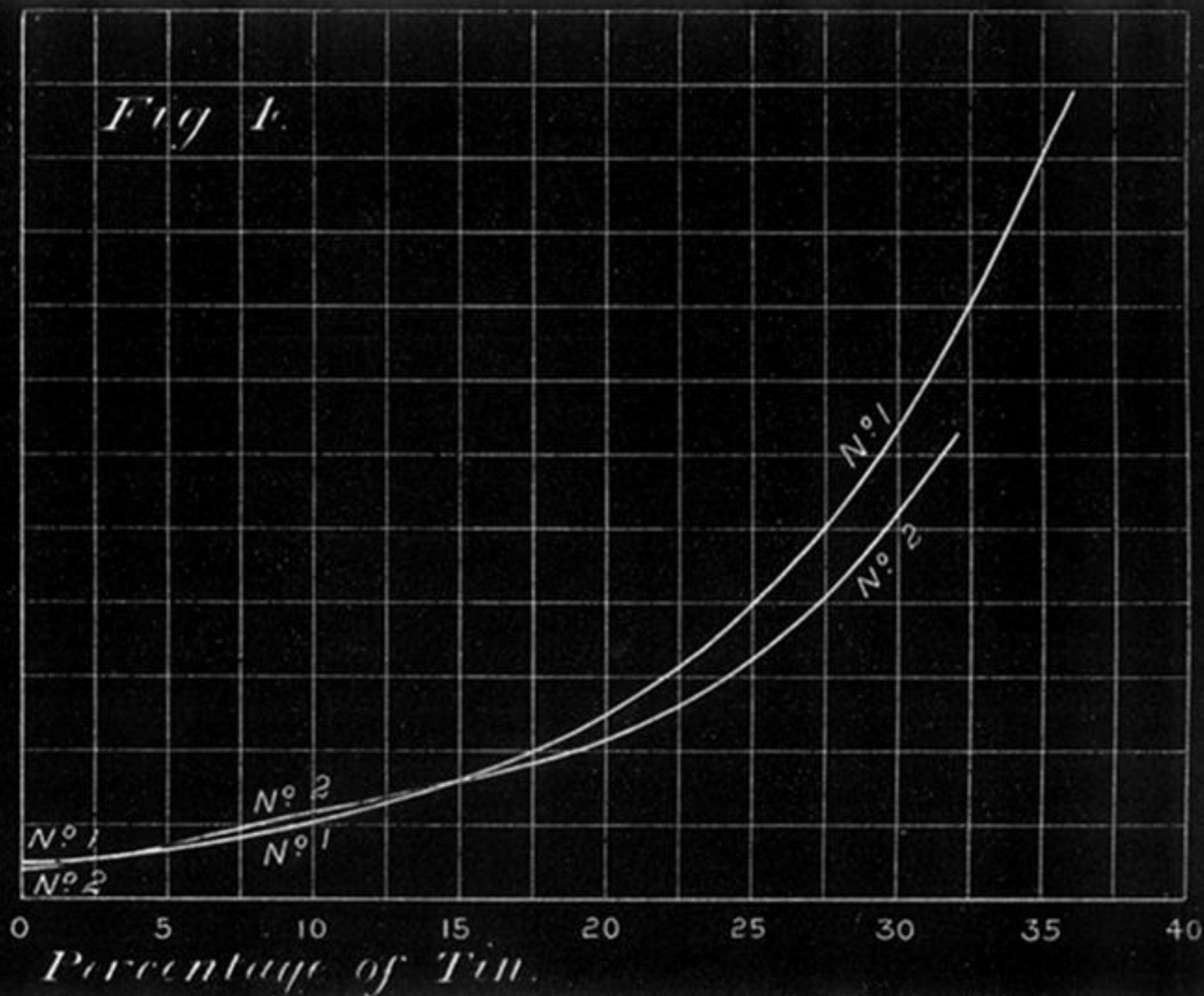
Fig. 2.





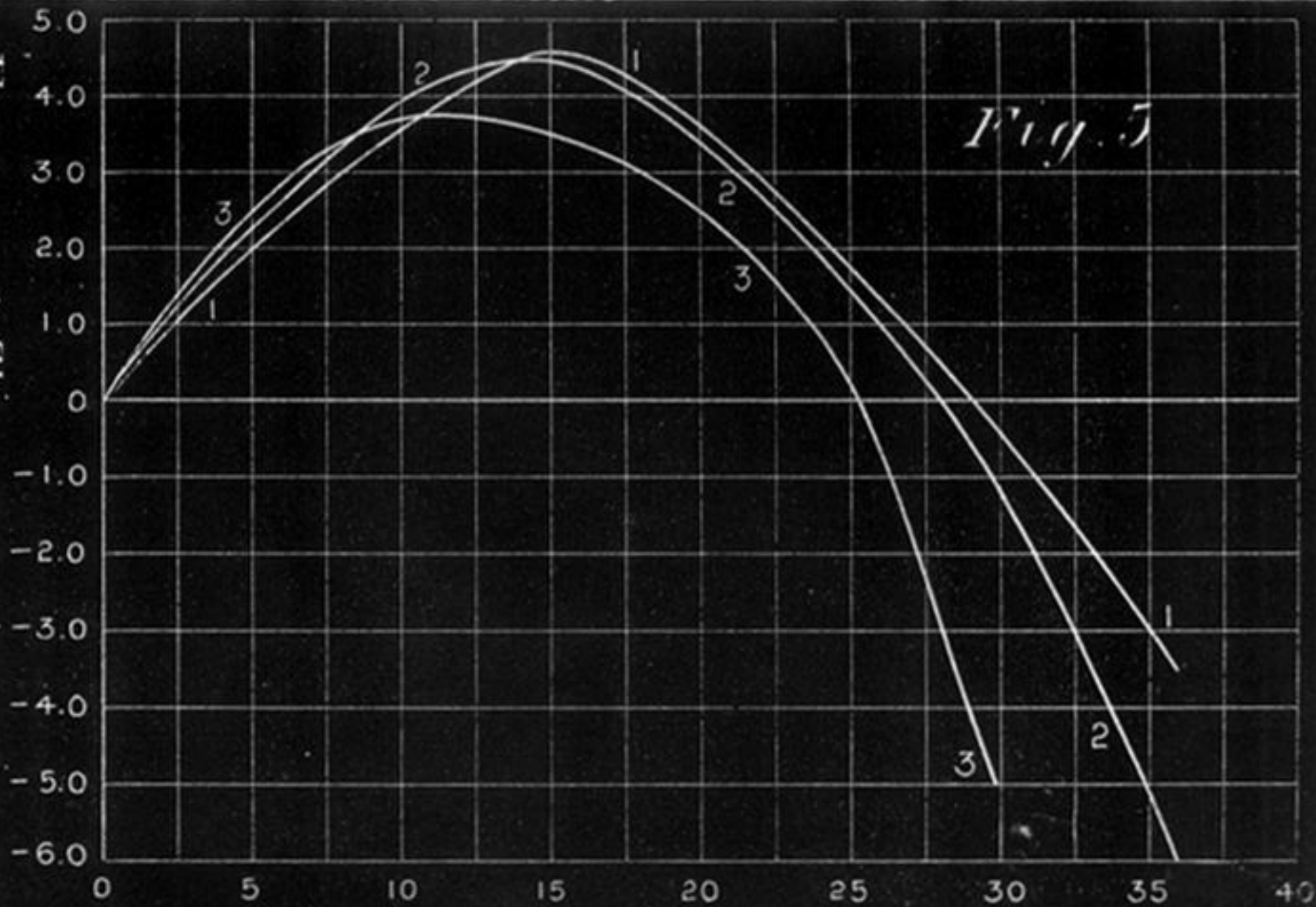
No. 1 Percentage of Zinc.
No. 2 " " Lead.

Fig 1.



*Excess of Tin percentage in
Lighter Alloy*

Fig. 5



Percentage of Tin in Heavier Alloy.